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COMPOSITION FOR THE OXIDATION DYEING OF KERATINOUS  
FIBRES AND DYEING PROCESS EMPLOYING THIS COMPOSITION

A subject-matter of the invention is a  
composition for the oxidation dyeing of keratinous  
5 fibres and in particular of human keratinous fibres,  
such as hair, comprising, in a medium appropriate for  
dyeing, at least one first oxidation base chosen from  
pyrazolo[1,5-a]pyrimidines, N,N-bis( $\beta$ -hydroxyethyl)-  
para-phenylenediamine as second oxidation base and at  
10 least one coupler chosen from meta-aminophenols and  
meta-phenylenediamines, and the dyeing process  
employing this composition.

It is known to dye keratinous fibres and in  
particular human hair with dyeing compositions  
15 comprising oxidation dye precursors, in particular  
ortho- or para-phenylenediamines, ortho- or para-  
aminophenols or heterocyclic bases, generally known as  
oxidation bases. Oxidation dye precursors or oxidation  
bases are colourless or weakly coloured compounds  
20 which, in combination with oxidizing substances, can  
give rise by an oxidative coupling process to coloured  
and colouring compounds.

It is also known that the shades obtained  
with these oxidation bases can be varied by combining  
25 them with couplers or colouring modifiers, the latter  
being chosen in particular from aromatic meta-diamines,  
meta-aminophenols, meta-diphenols and certain  
heterocyclic compounds.

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The variety of the molecules employed as oxidation bases and couplers makes it possible to obtain a rich palette of colours.

The so-called "permanent" colouring obtained  
5 by virtue of these oxidation dyes has, however, to satisfy a certain number of requirements. Thus, it must make it possible to obtain shades with the desired intensity and behave well in the face of external agents (light, bad weather, washing, permanent waving,  
10 perspiration or rubbing).

The dyes must also make it possible to cover white hair and, finally, be as unselective as possible, that is to say make it possible to obtain the least possible differences in colouring along the same  
15 keratinous fibre, this being because the latter can be sensitized (i.e. damaged) to a varying degree between its tip and its root.

Provision has already been made, in particular in Patent Application FR-A-2,750,048, for  
20 compositions for the oxidation dyeing of keratinous fibres comprising, as oxidation base, pyrazolo[1,5-a]-pyrimidines, optionally in combination with one or more couplers. However, the colourings obtained are not always powerful enough, chromatic enough or  
25 sufficiently resistant to the various attacks which hair may be subjected to.

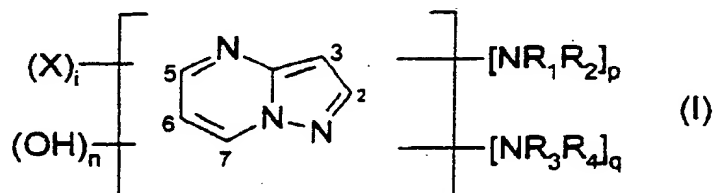
In point of fact, the Applicant Company has now just discovered that it is possible to obtain novel

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dyes, which dyes are capable of resulting in powerful colourings which are not very selective and which are highly resistant to the various attacks which the fibres may be subjected to, by combining at least one  
 5 pyrazolo[1,5-a]pyrimidine of formula (I) defined hereinbelow, as first oxidation base, N,N - bis ( $\beta$ -hydroxyethyl) - para-phenylenediamine and/or at least one of its addition salts with an acid, as second  
 10 suitably selected meta-aminophenols and from meta-phenylenediamines.

This discovery forms the basis of the present invention.

A first subject-matter of the invention is  
 15 therefore a composition for the oxidation dyeing of keratinous fibres and in particular of human keratinous fibres, such as hair, characterized in that it comprises, in a medium appropriate for dyeing:  
 - at least one first oxidation base chosen from  
 20 pyrazolo[1,5-a]pyrimidines of following formula (I) or their addition salts with an acid or with a base:



in which:

- $R_1, R_2, R_3$  and  $R_4$ , which are identical or different, denote a hydrogen atom, a  $(C_1-C_4)$ alkyl radical, an aryl radical, a hydroxy $(C_1-C_4)$ alkyl radical, a polyhydroxy $(C_2-C_4)$ alkyl radical, a  $(C_1-C_4)$ alkoxy $(C_1-C_4)$ -alkyl radical, an amino $(C_1-C_4)$ alkyl radical (it being possible for the amine to be protected by an acetyl, a ureido or a sulphonyl), a  $(C_1-C_4)$ alkylamino $(C_1-C_4)$ alkyl radical, a di $[(C_1-C_4)$ alkyl]amino $(C_1-C_4)$ alkyl radical (it being possible for the dialkyls to form a 5- or 6-membered aliphatic or heterocyclic ring), a hydroxy $(C_1-C_4)$ alkylamino $(C_1-C_4)$ alkyl radical or a di[hydroxy $(C_1-C_4)$ alkyl]amino $(C_1-C_4)$ alkyl radical;
- the X radicals, which are identical or different, denote a hydrogen atom, a  $(C_1-C_4)$ alkyl radical, an aryl radical, a hydroxy $(C_1-C_4)$ alkyl radical, a polyhydroxy $(C_2-C_4)$ alkyl radical, an amino $(C_1-C_4)$ alkyl radical, a  $(C_1-C_4)$ alkylamino $(C_1-C_4)$ alkyl radical, a di $[(C_1-C_4)$ alkyl]amino $(C_1-C_4)$ alkyl radical (it being possible for the dialkyls to form a 5- or 6-membered aliphatic or heterocyclic ring), a hydroxy $(C_1-C_4)$ alkylamino $(C_1-C_4)$ alkyl radical, a di[hydroxy $(C_1-C_4)$ alkyl]amino $(C_1-C_4)$ alkyl radical, an amino radical, a  $(C_1-C_4)$ alkylamino radical, a di $[(C_1-C_4)$ alkyl]amino radical, a halogen atom, a carboxylic acid group or a sulphonic acid group;
- i has the value 0, 1, 2 or 3;
- p has the value 0 or 1;
- q has the value 0 or 1;

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- n has the value 0 or 1;

with the proviso that:

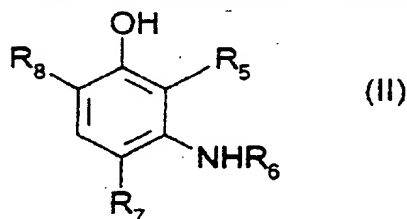
-(i) the sum  $p + q$  is other than 0;

-(ii) when  $p + q$  is equal to 2, then n has the value 0

5 and the  $NR_1R_2$  and  $NR_3R_4$  groups occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;

-(iii) when  $p + q$  is equal to 1, then n has the value 1 and the  $NR_1R_2$  (or  $NR_3R_4$ ) group and the OH group occupy the (2,3), (5,6), (6,7), (3,5) or (3,7) positions;

- 10 - at least one second oxidation base chosen from N,N-bis( $\beta$ -hydroxyethyl)- para-phenylenediamine and its addition salts with an acid; and
- at least one coupler chosen from meta-phenylenediamines and meta-aminophenols of following
- 15 formula (II) and their addition salts with an acid:



in which:

- $R_5$  and  $R_8$ , which are identical or different, represent a hydrogen atom, a halogen atom, such as chlorine, bromine, iodine or fluorine, or a  $(C_1-C_4)$ alkyl, monohydroxy $(C_1-C_4)$ alkyl, polyhydroxy $(C_2-C_4)$ alkyl,  $(C_1-C_4)$ alkoxy, monohydroxy $(C_1-C_4)$ alkoxy or polyhydroxy $(C_2-C_4)$ alkoxy radical;
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- R<sub>6</sub> represents a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl, polyhydroxy(C<sub>2</sub>-C<sub>4</sub>)alkyl or amino(C<sub>1</sub>-C<sub>4</sub>)alkyl radical;
- R<sub>7</sub> represents a hydrogen atom, a (C<sub>1</sub>-C<sub>4</sub>)alkyl or (C<sub>1</sub>-C<sub>4</sub>)alkoxy radical or a halogen atom chosen from chlorine, bromine or fluorine;

it being understood that, when R<sub>5</sub> represents a chlorine atom and when R<sub>6</sub> and R<sub>7</sub> simultaneously represent a hydrogen atom, then R<sub>8</sub> is other than a methyl radical.

10           The dyeing composition in accordance with the invention results in powerful and chromatic colourings which exhibit low selectivity and excellent properties of resistance both with respect to atmospheric agents, such as light and bad weather, and with respect to  
15           perspiration and various treatments which hair may be subjected to.

Another subject-matter of the invention is a process for the oxidation dyeing of keratinous fibres employing this dyeing composition.

20           The pyrazolo[1,5-a]pyrimidines of formula (I) which can be used as first oxidation base in the dyeing composition in accordance with the invention are known compounds which are disclosed in Patent Application FR-A-2,750,048, the contents of which form an integral  
25           part of the present application.

Mention may in particular be made, among the pyrazolo[1,5-a]pyrimidines of formula (I) which can be

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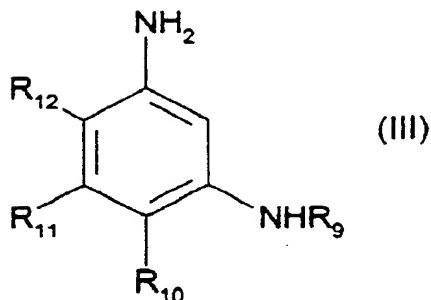
used as oxidation base in the dyeing compositions in accordance with the invention, of:

- pyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2-methylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 5 - 2,5-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- pyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 2,7-dimethylpyrazolo[1,5-a]pyrimidine-3,5-diamine;
- 3-aminopyrazolo[1,5-a]pyrimidin-7-ol;
- 3-amino-5-methylpyrazolo[1,5-a]pyrimidin-7-ol;
- 10 - 3-aminopyrazolo[1,5-a]pyrimidin-5-ol;
- 2-(3-aminopyrazolo[1,5-a]pyrimidin-7-ylamino)ethanol;
- 3-amino-7-( $\beta$ -hydroxyethylamino)-5-methylpyrazolo-  
[1,5-a]pyrimidine;
- 2-(7-aminopyrazolo[1,5-a]pyrimidin-3-ylamino)ethanol;
- 15 - 2-[(3-aminopyrazolo[1,5-a]pyrimidin-7-yl)(2-hydroxy-  
ethyl)amino]ethanol;
- 2-[(7-aminopyrazolo[1,5-a]pyrimidin-3-yl)(2-hydroxy-  
ethyl)amino]ethanol;
- 5,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 20 - 2,6-dimethylpyrazolo[1,5-a]pyrimidine-3,7-diamine;
- 2,5,N-7,N-7-tetramethylpyrazolo[1,5-a]pyrimidine-3,7-  
diamine;

and their addition salts with an acid or with a base.

The meta-phenylenediamines which can be used  
25 as coupler in the dyeing composition in accordance with  
the invention are preferably chosen from the compounds  
of following formula (III) and their addition salts  
with an acid:

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in which:

- R<sub>9</sub> represents a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl or polyhydroxy(C<sub>2</sub>-C<sub>4</sub>)alkyl radical;
- R<sub>10</sub> and R<sub>11</sub>, which are identical or different, represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkoxy or polyhydroxy(C<sub>2</sub>-C<sub>4</sub>)alkoxy radical;
- R<sub>12</sub> represents a hydrogen atom, a (C<sub>1</sub>-C<sub>4</sub>)alkoxy, amino(C<sub>1</sub>-C<sub>4</sub>)alkoxy, monohydroxy(C<sub>1</sub>-C<sub>4</sub>)alkoxy or polyhydroxy(C<sub>2</sub>-C<sub>4</sub>)alkoxy radical or a 2,4-diaminophenoxyalkoxy radical.

Mention may more particularly be made, among the meta-phenylenediamines of formula (III) above, of meta-phenylenediamine, 3,5-diamino-1-ethyl-2-methoxybenzene, 3,5-diamino-2-methoxy-1-methylbenzene, 2,4-diamino-1-ethoxybenzene, 1,3-bis(2,4-diaminophenoxy)propane, bis(2,4-diaminophenoxy)methane, 1-(β-aminoethyloxy)-2,4-diaminobenzene, 2-amino-1-(β-hydroxyethyloxy)-4-(methylamino)benzene, 2,4-diamino-1-ethoxy-5-methylbenzene, 2,4-diamino-5-(β-hydroxyethyloxy)-1-methylbenzene, 2,4-diamino-



1-( $\beta,\gamma$ -dihydroxypropyloxy)benzene, 2,4-diamino-1-( $\beta$ -hydroxyethyloxy)benzene, 2-amino-4-N-( $\beta$ -hydroxyethyl)amino-1-methoxybenzene and their addition salts with an acid.

5                   Mention may more particularly be made, among the meta-aminophenols of formula (II) which can be used as coupler in the dyeing composition in accordance with the invention, of meta-aminophenol, 5-amino-2-methoxyphenol, 5-amino-2-( $\beta$ -hydroxyethyloxy)phenol,  
 10 5-amino-2-methylphenol, 5-N-( $\beta$ -hydroxyethyl)amino-2-methylphenol, 5-N-( $\beta$ -hydroxyethyl)amino-4-methoxy-2-methylphenol, 5-amino-4-methoxy-2-methylphenol, 5-amino-4-chloro-2-methylphenol, 5-amino-2,4-dimethoxyphenol, 5-( $\gamma$ -hydroxypropylamino)-  
 15 2-methylphenol, 3-amino-6-chlorophenol, 3-amino-6-bromophenol, 3-( $\beta$ -aminoethyl)amino-6-chlorophenol, 3-( $\beta$ -hydroxyethyl)amino-6-chlorophenol and their addition salts with an acid.

                  The pyrazolo[1,5-a]pyrimidine or  
 20 pyrazolo[1,5-a]pyrimidines of formula (I) in accordance with the invention and/or the addition salt or their addition salts with an acid or with a base preferably represent from 0.0005 to 12% by weight approximately of the total weight of the dyeing composition in  
 25 accordance with the invention and more preferably still from 0.005 to 6% by weight approximately of this weight.

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N,N -Bis( $\beta$ -hydroxyethyl)- para-phenylene-diamine and/or the addition salt or its addition salts with an acid which can be used as second oxidation base in the dyeing composition in accordance with the

5 invention preferably represent from 0.0005 to 12% by weight approximately of the total weight of the dyeing composition in accordance with the invention and more preferably still from 0.005 to 6% by weight approximately of this weight.

10 The meta-phenylenediamine or meta-phenylenediamines and/or the meta-aminophenol or meta-aminophenols of formula (II) and/or the addition salt or their addition salts with an acid preferably represent from 0.0001 to 10% by weight approximately of  
15 the total weight of the dyeing composition and more preferably still from 0.005 to 5% by weight approximately of this weight.

The dyeing composition in accordance with the invention can additionally comprise one or more  
20 couplers other than the meta-phenylenediamines and the meta-aminophenols of formula (II) and/or one or more direct dyes, in particular for modifying the shades or enriching them with highlights.

Mention may in particular be made, among the  
25 couplers which can additionally be present in the dyeing composition according to the invention, of meta-diphenols, heterocyclic couplers and their addition salts with an acid.

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Generally, the addition salts with an acid which can be used in the context of the dyeing compositions of the invention (oxidation bases and couplers) are chosen in particular from hydrochlorides, hydrobromides and sulphates and tartrates, lactates and acetates. The addition salts with a base which can be used in the context of the dyeing compositions of the invention are in particular those obtained with sodium hydroxide, potassium hydroxide, aqueous ammonia or amines.

The medium appropriate for dyeing (or vehicle) of the dyeing composition in accordance with the invention is generally composed of water or of a mixture of water and of at least one organic solvent, in order to dissolve the compounds which would not be sufficiently soluble in water. Mention may be made, for example, as organic solvent, of C<sub>1</sub>-C<sub>4</sub> alkanols, such as ethanol and isopropanol; glycerol; glycols and glycol ethers, such as 2-butoxyethanol, propylene glycol, propylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monomethyl ether; and aromatic alcohols, such as benzyl alcohol or phenoxyethanol, the analogous products and their mixtures.

The solvents can be present in proportions preferably of between 1 and 40% by weight approximately with respect to the total weight of the dyeing

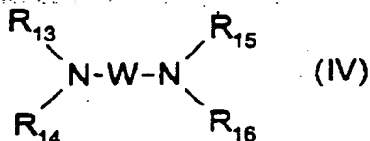
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composition and more preferably still between 5 and 30% by weight approximately.

The pH of the dyeing composition in accordance with the invention is generally between 3 and 12 approximately and preferably between 5 and 12 approximately. It can be adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibres.

Mention may be made, among acidifying agents, by way of example, of inorganic or organic acids, such as hydrochloric acid, orthophosphoric acid, sulphuric acid, carboxylic acids, such as acetic acid, tartaric acid, citric acid or lactic acid, or sulphonc acids.

Mention may be made, among basifying agents, by way of example, of aqueous ammonia, alkaline carbonates, alkanolamines, such as mono-, di- and triethanolamines, 2-methyl-2-aminopropanol and their derivatives, sodium hydroxide, potassium hydroxide and the compounds of following formula (IV):



in which W is a propylene residue optionally substituted by a hydroxyl group or a (C<sub>1</sub>-C<sub>4</sub>)alkyl radical and R<sub>13</sub>, R<sub>14</sub>, R<sub>15</sub> and R<sub>16</sub>, which are identical or different, represent a hydrogen atom or a (C<sub>1</sub>-C<sub>4</sub>)alkyl or hydroxy(C<sub>1</sub>-C<sub>4</sub>)alkyl radical.

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The dyeing composition in accordance with the invention can also include various adjuvants conventionally used in hair dyeing compositions, such as anionic, cationic, non-ionic, amphoteric or  
5 zwitterionic surface-active agents or their mixtures, anionic, cationic, non-ionic, amphoteric or zwitterionic polymers or their mixtures, inorganic or organic thickening agents, such as, for example, non-ionic guar gums, antioxidizing agents, enzymes, such as  
10 2-electron oxidoreductases, peroxidases or laccases, penetration agents, sequestering agents, fragrances, buffers, dispersing agents, conditioning agents, such as, for example, volatile or nonvolatile and modified or unmodified silicones, film-forming agents,  
15 ceramides, preserving agents or opacifying agents.

Of course, a person skilled in the art will take care to choose this or these optional additional compound or compounds so that the advantageous properties intrinsically attached to the dyeing  
20 composition in accordance with the invention are not, or not substantially, detrimentally affected by the envisaged addition or additions.

The dyeing composition in accordance with the invention can be provided in various forms, such as in  
25 the form of liquids, powders, creams or gels, which are optionally pressurized, or in any other form appropriate for carrying out dyeing of keratinous fibres and in particular human hair.

Another subject-matter of the invention is a process for dyeing keratinous fibres and in particular human keratinous fibres, such as hair, employing the dyeing composition as defined above.

5           According to this process, the dyeing composition as defined above is applied to the fibres, the colour being developed at acidic, neutral or alkaline pH using an oxidizing agent which is added only at the time of use to the dyeing composition or  
10 which is present in an oxidizing composition applied simultaneously or sequentially in a separate fashion.

          According to a particularly preferred embodiment of the dyeing process according to the invention, the dyeing composition described above is  
15 mixed, at the time of use, with an oxidizing composition comprising, in a medium appropriate for dyeing, at least one oxidizing agent present in an amount sufficient to develop a colouring. The mixture obtained is subsequently applied to the keratinous  
20 fibres and is left to stand for 3 to 50 minutes approximately, preferably 5 to 30 minutes approximately, after which the hair is rinsed, washed with a shampoo, rinsed again and dried.

          The oxidizing agent present in the oxidizing  
25 composition as defined above can be chosen from oxidizing agents conventionally used for the oxidation dyeing of keratinous fibres and among which may be mentioned hydrogen peroxide, urea hydrogen peroxide,

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alkali metal bromates, persalts, such as perborates and persulphates, peracids or enzymes, such as 2-electron oxidoreductases, peroxidases and laccases. Hydrogen peroxide is particularly preferred.

5           The pH of the oxidizing composition including the oxidizing agent as defined above is such that, after mixing with the dyeing composition, the pH of the resulting composition applied to keratinous fibres preferably varies between 3 and 12 approximately and  
10 more preferably still between 5 and 11. It is adjusted to the desired value by means of acidifying or basifying agents commonly used in dyeing keratinous fibres and as defined above.

          The oxidizing composition as defined above  
15 can also include various adjuvants conventionally used in hair dyeing compositions and as defined above.

          The composition which is finally applied to keratinous fibres can be provided in various forms, such as in the form of liquids, creams or gels, or in  
20 any other form appropriate for carrying out dyeing of keratinous fibres and in particular of human hair.

          Another subject-matter of the invention is a dyeing multi-compartment device or kit or any other packaging system with several compartments, a first  
25 compartment of which includes the dyeing composition as defined above and a second compartment of which includes the oxidizing composition as defined above. These devices can be equipped with a means allowing the

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desired mixture to be deposited on the hair, such as the devices disclosed in Patent FR-2,586,913 on behalf of the Applicant Company.

The examples which follow are intended to illustrate the invention without, however, limiting the scope thereof.

### EXAMPLES

#### DYEING EXAMPLES 1 AND 2

The following dyeing compositions were prepared (contents in grams):

EXAMPLE	1	2
Pyrazolo[1,5-a]pyrimidine-3,7-diamine·2HCl	0.666	0.666
N,N -Bis(β-hydroxyethyl) - para-phenylenediamine	0.936	0.936
2-Methyl-5- [N- (β-hydroxyethyl) amino]phenol	1.0	-
2,4-Diamino-1- (β-hydroxyethyloxy) benzene·2HCl	-	1.446
Common dyeing vehicle	(*)	(*)
Demineralized water, q.s. for	100 g	100 g

(\*): Common dyeing vehicle:

- 96° Ethyl alcohol 18 g
- Pentasodium salt of diethylenetriamine-pentaacetic acid 1.1 g
- 15 - Aqueous ammonia comprising 20% of NH<sub>3</sub> 10 g

At the time of use, each of the dyeing compositions described above was mixed, weight for weight, with a 20-volume hydrogen peroxide solution (6% by weight).

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Each of the mixtures thus prepared was applied for 30 minutes to locks of natural grey hair comprising 90% of white hairs. The locks were subsequently rinsed, washed with a standard shampoo, 5 rinsed again and then dried.

The hair was dyed in a shade which appears in the table below:

EXAMPLE	SHADE OBTAINED
1	Deep ash purple
2	Blue

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